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SULPHATION CAPACITY OF ALBERTA LIMESTONES

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MICROMEDIA

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by

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ABSTRACT

Seven limestone samples from five locations in Alberta were evaluated in a bench-scale fluidized bed reactor to determine their performance as SO_2 sorbents in fluidized bed combustors (FBC). The rocks were tested in the 0.841-1.00 mm size and as pellets made from -0.149 mm particle material simulating the behaviour in a bubbling FBC and a circulating FBC. The sulphation capacity is 18-25% for the "coarse" rocks and 48-63% for the pellets.

POUVOIR DE SULFATATION DES CALCAIRES DE L'ALBERTA

par

C.A. Hamer*

RÉSUMÉ

Sept échantillons de calcaire provenant de cinq endroits en Alberta ont été évalués dans un réacteur à lit fluidisé, en banc d'essai, pour déterminer leur performance à titre d'absorbants de SO_2 pour la combustion en lit fluidisé. Les essais ont été conduits avec des particules de roche dont la granulométrie était comprise entre 0,841 et 1,00 mm ainsi que des boulettes constituées de particules de granulométrie inférieure à 0,149 mm afin de simuler le comportement dans un four de combustion en lit fluidisé à bulles et circulant. Le pouvoir de sulfatation s'établit entre 18 et 25 % pour les roches "grossières" et entre 48 et 63 % pour les boulettes.

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INTRODUCTION

As part of the AOSTRA/Industry Upgrading Residue Utilization Project, consideration is being given to the use of fluidized bed combustion (FBC) to recover energy from residues. In fluidized bed technology limestone is used as the bed material, principally because it captures sulphur dioxide emitted during combustion. The efficiency of the limestone as an SO_2 sorbent is very dependent upon the physical and chemical composition of the rock (1). The sulphation reaction takes place at the surface and in the pores of the sorbent material; therefore, the more porous the rock and the finer the particle size, the greater will be the sulphation capacity.

There are essentially two types of atmospheric fluid beds: the bubbling bed and the circulating bed. The former utilizes limestone in the size range 3-0.5 mm whereas the latter uses material of -0.15 mm size. The efficiency of sorbent utilization is much greater in the circulating FBC. The most practical method of evaluating the limestone efficiency as a sorbent, other than a full-scale test, is by thermogravimetric analysis or in a bench-scale fluidized bed reactor. The latter more closely approximates the actual conditions to which limestone is exposed in FBC. To predict sorbent behaviour in a bubbling bed, limestone particles are tested in the size range 1.00-0.841 mm. The -0.15 mm material is pelletized to prevent loss by elutriation prior to testing. It is reasonable to believe that the results of the pellet testing are indicative of expected behaviour in a circulating FBC.

This report is a compilation of the fluidized bed reactor test work on Alberta limestones.

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PROCEDURE

LIMESTONE SAMPLES

The rock samples from Alberta were collected from a variety of sources as listed below.

CS-1 Sample from outcrop at Clausen's Landing on the Athabasca River. Supplied by C.F. Lamb, Sr. Geologist, Canstar Oil Sands Ltd. 1981.

SY-1 Sample from outcrop where Beaver Creek crosses Provincial Highway 963, Fort McMurray. Supplied by H.D. O'Donnell, Section Head, Geology, Suncrude Canada Ltd. 1981.

SY-2 Grab sample taken during the quarrying of 50 t in March, 1983, same location as SY-2, by Dean Wallace, Alberta Research Council.

Alt-4, Alt-5 Two samples from Steele Brothers (Canada) Ltd. quarry at Enshaw, July 7, 1983. Supplied by B. Clements, Combustion Engineering Ltd.

Alt-6 Sample from beneath tar sands mining pit at Suncor. Supplied by D. Scoulding, Monenco, 1984.

Alt-7 Sample from Genstar Cement Ltd. quarry at Cadomin. Supplied by D. Scoulding, Monenco, 1984.

SAMPLE PREPARATION

The quantity of sample received varied from 5-40 kg. The rock was reduced to the desired size range in a jaw crusher, gyratory cone crushers and a disc pulverizer. A representative sample was taken for chemical analysis. The material was sieved to obtain the 1.00-0.841 mm size fraction which is the standard for sulphation tests. The -0.149 mm material was blended with bentonite, nominally 2 mass %, and agglomerated on a disc pelletizer. The oven dried pellets were sieved to give the 1.00-0.841 mm size for testing.

SULPHATION TESTS

The fluidized bed reactor test procedure has been described in detail in Reference 1. In summary, a weighed quantity of limestone is injected into a bed of silica sand maintained at 850°C and fluidized by synthetic flue gas containing 0.3% SO₂, 5% O₂, 8% CO₂, with the balance N₂. The SO₂ concentration in the off-gas is continuously analysed with a Beckman infrared analyser. Within a minute of adding the limestone the SO₂ concentration drops to a fraction of the inlet value. It then begins to increase, the rate being dependent upon the particular limestone, until after one to three hours the exhaust SO₂ concentration is constant at or very near the inlet concentration. From this curve, the SO₂ feed rate and the CaCO₃ content, the sulphation capacity and an equation describing the sulphation behaviour of the limestone can be determined.

RESULTS AND DISCUSSION

SAMPLE COMPOSITION

Table 1 gives the CaCO₃ content of the rock samples. The samples from the commercial quarries are the purer limestones. The Syncrude and Suncor samples, both from the Fort McMurray area, are contaminated with clay minerals. Although these samples were not subject to complete analysis, the presence of clay was obvious from their behaviour during pelletizing.

Table 1. CaCO₃ content of Alberta limestones

Sample	% CaCO ₃	
CS-1	90.1	
SY-1	91.3	
SY-2	75.6	
Alt-4	97	Analysis supplied by CE
Alt-5	97	Analysis supplied by CE
Alt-6	65.6	
Alt-7	93.4	

SULPHATION CAPACITY

The sulphation capacities of the natural rock and pellets are given in Table 2. The sulphation capacity, X , of the limestone is described by the equation:

$$X = a[1 - \exp(-kt^n)]$$

where "a", "k" and "n" are parameters whose value is particular to a limestone. They are used in modelling fluidized bed combustors.

Table 2. Sulphation capacity of Alberta limestones, 1.00-0.841 mm

Sample	X	Rock			Size, μm (mean vol)
		a	k	n	
CS-1	25.6	26.429	.0460	.9522	
SY-1	19.8	20.068	.1081	.8034	
SY-2	22.3	22.460	.0780	.9668	
Alt-4	18.5	21.046	.1176	.6445	
Alt-5	18.0	18.197	.1674	.7650	
Alt-6	24.3	24.326	.2192	.6780	
Alt-7	20.6	21.053	.1387	.7526	
Pellet					
SY-2	58.9	59.497	.0323	1.142	24.0
Alt-4	48.4	49.606	.0342	1.033	15.1
Alt-5	54.8	56.622	.0268	1.074	16.6
Alt-6	62.5	61.791	.0364	1.081	26.2
Alt-7	56.6	57.300	.0314	1.022	35.3

The sulphation capacities of the rock samples in the 1.0 mm size range are all quite similar. CS-1 is the best sorbent but none are very good. On the other hand, pellets of finely ground limestone give excellent sulphation capacities. These pellets all used bentonite as the binder in order not to affect the sulphation capacity. Other test work, not reported here, has shown that pelletizing with sodium carbonate as the binder produces stronger pellets with enhanced sulphation capacity compared to those prepared with bentonite (2).

ATTRITION

No specific test was used to measure attrition or decrepitation due to thermal shock. An indication of the breakdown of material is given by observing the quantity of cyclone dust collected. In no case was the amount of dust considered excessive. A quantitative measurement was not made because of contamination of this dust with some sand bed material.

PREDICTING SORBENT PERFORMANCE

Although the sulphation capacity is a good indication of limestone performance, the use of this data in the Argonne National Laboratory model permits a graphical representation of the limestone behaviour in an FBC. The physical parameters and operating conditions of the FBC unit at CFB Summerside were used for the model. These conditions are listed in Table 3. The graph of SO₂ retention versus the kg of limestone required per kg of 5% sulphur fuel is given as Fig. 1. Those few samples not graphed fall within the ranges of those shown. For fuels with different sulphur contents, the values taken from the graph may be adjusted proportionally. The effect of particle size is obvious by comparing the curves for the pellets with the natural rock. The quantity of limestone as pellets, or finely ground material, is about one-third that of the coarser material for the same SO₂ retention. The curves indicate that the behaviour of all the Alberta rocks tested are similar within the limits of sampling, testing and modelling.

Table 3. Operating conditions, FBC unit at CFB Summerside

Temperature: 850°C
 Pressure: 101 kPa
 Fluidizing velocity: 1.83 m/s
 Static bed height: 0.6 m
 Expanded bed height: 1.5 m
 Area of bed: 3.52 sq m (A bed)
 Number of openings in distributor: 300 (actually 274)
 Fuel feed rate: 1100 kg/h
 Sulphur content of fuel: 5%
 Sorbent particle size: 1.0 mm

CONCLUSION

As sorbents for SO_2 in atmospheric bubbling FBC units, the Alberta limestones are all quite similar to each other and would be rated as "fair" sorbents. However, as finely ground material agglomerated into pellets or as fine particles in a circulating FBC, all samples would be excellent sorbents.

REFERENCES

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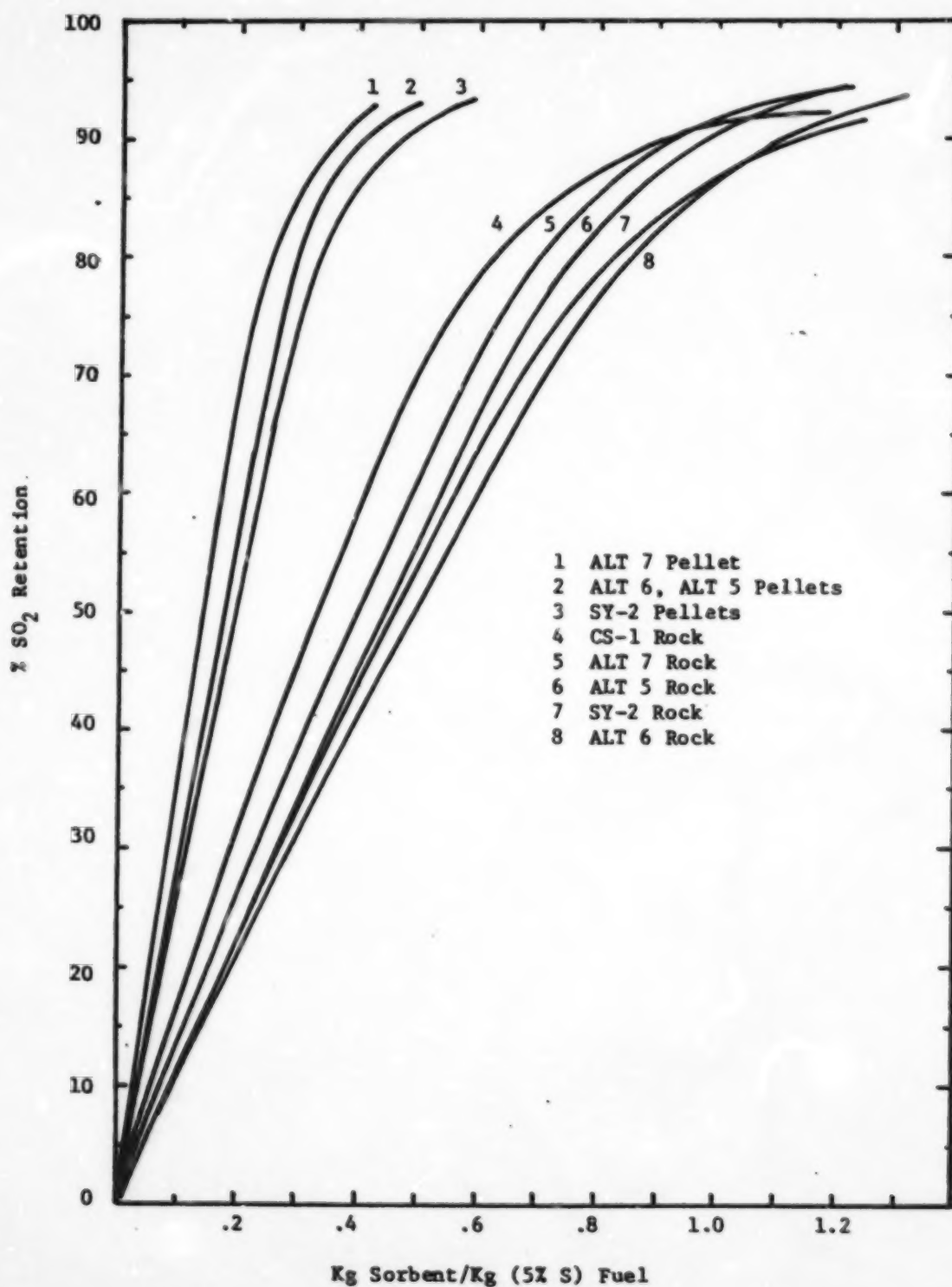


Fig. 1 - Predicted quantity of Alberta limestone required for the Summerside AFBC combusting 5% S fuel